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Aluminum selenite trihydrate, synthetic, $M_r = 488.88$, trigonal, $R32$, $a = 8.3806$ (4) Å, $\alpha = 65.527$ (3)°, $V = 466.2$ Å^3, $Z = 2$, $D_x = 3.48$g/cm^3, λ(Mo Kα) = 0.71073 Å, μ = 119.7 cm^{-1}, $F(000) = 460$, $T = 298$ (2) K, $R = 4.48\%$, $R_w = 5.10\%$ for 556 observed reflections with $I > 3\sigma(I)$. Synthesized hydrothermally, $Al_2(SeO_3)_3 \cdot 3H_2O$ consists of a 3-dimensional network of vertex-sharing octahedral AlO_6 and pyramidal SeO_3 groups, connected *via* Al-O-Se links. The three water molecules are coordinated by one of the aluminum atoms. The title compound is isostructural with $Ga_2(SeO_3)_3 \cdot 3H_2O$ and $Cr_2.(SeO_3)_3 \cdot H_2O$, and is closely related to aluminum selenite hexahydrate, $Al_2(SeO_3)_3 \cdot 6H_2O$.

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The Synthesis and Crystal Structure of Aluminum Selenite Trihydrate, $Al_2(SeO_3)_3 \cdot 3H_2O$

by

W.T.A. Harrison, G.D. Stucky, R.E. Morris, and A.K. Cheetham

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The Synthesis and Crystal Structure of Aluminum Selenite Trihydrate, $Al_2(SeO_3)_3 \cdot 3H_2O$

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Abstract. Aluminum selenite trihydrate, synthetic, $M_r = 488.88$, trigonal, $R32$, $a = 8.3806(4)$ Å, $\alpha = 65.527(3)°$, $V = 466.2$ Å^3, $Z = 2$, $D_x = 3.48$ g/cm^3, λ(Mo Kα) = 0.71073 Å, $\mu = 119.7$ cm^{-1}, $F(000) = 460$, $T = 298(2)$ K, $R = 4.48\%$, $R_w = 5.10\%$ for 556 observed reflections with $I > 3\sigma(I)$. Synthesized hydrothermally, $Al_2(SeO_3)_3 \cdot 3H_2O$ consists of a 3-dimensional network of vertex-sharing octahedral AlO_6 and pyramidal SeO_3 groups, connected *via* Al–O–Se links. The three water molecules are coordinated by one of the aluminum atoms. The title compound is isostructural with $Ga_2(SeO_3)_3 \cdot 3H_2O$ and $Cr_2(SeO_3)_3 \cdot 3H_2O$, and is closely related to aluminum selenite hexahydrate, $Al_2(SeO_3)_3 \cdot 6H_2O$.

Introduction: In the solid-state, the selenium(IV)-containing selenite ion, SeO_3^{2-} shows a characteristic pyramidal coordination due to its (unobserved) $4s^2$ hybridized lone pair of electrons. As yet, there are few well defined structural families of selenites, but a number of phases containing a trivalent, octahedral metal ion, M^{3+}, selenite, SeO_3^{2-} and/or hydrogen selenite $HSeO_3^-$, and possibly water, have been studied by single crystal X-ray diffraction methods, including: $Mn_2(SeO_3)_3 \cdot 3H_2O$ (Koskenlinna and Valkonen, 1977); $FeH(SeO_3)_2$ (Valkonen and Koskenlinna, 1978); $Sc(HSeO_3)_3$ (Valkonen and Leskelã, 1978); $Ga_2(SeO_3)_3 \cdot 3H_2O$ Rastsvetaeva, Andrianov and Volodnia, 1986); $Fe(Se_2O_5)(HSeO_3)$ and $Fe(HSeO_3)_3$ (Muilu and Valkonen, 1987); $Al_2(SeO_3)_3 \cdot 6H_2O$ and $Al(SeO_3)(HSeO_3) \cdot 2H_2O$ (Morris, Harrison, Stucky and Cheetham, 1991); and $Cr_2(SeO_3)_3 \cdot 3H_2O$ and $InH(SeO_3)_2$ (Harrison, McManus, Stucky and Cheetham, 1991). Here we report the preparation and crystal structure of $Al_2(SeO_3)_3 \cdot 3H_2O$.

Experimental: The title compound was synthesised hydrothermally from the starting materials $Al(NO_3)_3 \cdot 9H_2O$ (Fisher, 2 g) and excess SeO_2 (Aldrich, 5 g) in 15 cm^3 of water. The teflon-lined steel bomb was heated to 473 (5) K for 48 hours and cooled to room temperature overnight. An estimated maximum pressure of 3 MPa was achieved. Transparent, rhombic crystals with linear dimensions of up to 0.5 mm were recovered from the reaction mixture.

An irregular crystal, dimensions *ca.* 0.12 × 0.12 × 0.12 mm was mounted on a Huber automated diffractometer. The unit cell constants were determined and refined from 14 centered reflections ($18° < 2\theta < 24°$). Data were collected at room temperature (298 (2) K) in the θ-2θ scan mode (scan speed = $6° \, min^{-1}$) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) over the range $0 < 2\theta \leq 65°$ for $-6 \leq h \leq 9$, $-5 \leq k \leq 10$, $1 \leq l \leq 12$, $(\sin\theta/\lambda)_{max} = 0.76$), with regular checks on reflection intensity (every 100 reflections; no variation observed), absorption correction based on ψ-scans of reflections

with $\chi \sim 90°$ (min. 1.0, max. 1.2) applied during data reduction. There were no systematic absences, consistent with five distinct trigonal space groups: $R3$, $R\bar{3}$, $R32$, $R3m$ and $R\bar{3}m$. 2293 reflections were measured, of which 556 were used in the structure solution and refinement (merging $R = 6.6\%$; reflections with $I < 3\sigma(I)$ considered unobserved).

The initial model, in the rhombohedral setting of space group $R32$ (No. 155), was taken from our study of the isostructural chromium selenite trihydrate (Harrison, McManus, Stucky and Cheetham, 1991), and the usual atomic positional and anisotropic thermal parameters were refined to convergence. For the final cycle of full matrix anisotropic refinement against F: 53 parameters, origin defined as centroid of structure (Waser, 1974), Σ(shift/e.s.d.) = 0.01, $R = 4.48\%$, $wR = 5.10\%$ (3-term Chebyshev weighting scheme (Carruthers and Watkin, 1979) with coefficients 24(6), -11(7) and 11(5) where the digit in parentheses is the e.s.d.), maximum residual electron density = $2\,e\,A^{-3}$ near O(4), no proton positions located. Structure refinement and analysis was carried out using the Oxford CRYSTALS system (Watkin, Carruthers and Betteridge, 1985) on a μVAX-II computer. Complex, neutral-atom scattering-factors were taken from *International Tables for X-Ray Crystallography* (1974). An isotropic secondary extinction correction (Larson, 1970: refined value = 46(4)) was also applied.

Discussion: Table 1* gives final atomic positional and thermal parameters for $Al_2(SeO_3)_3 \cdot 3H_2O$, and Table 2 gives selected bond distance/angle data for this phase. The structure of aluminum selenite trihydrate (Figure 1) consists of a 3-dimensional network of vertex-sharing AlO_6 and SeO_3 groups linked *via* Al–O–Se bonds: there are two crystallographically-distinct aluminum atoms, one selenium atom and four oxygen atoms, one of which (O(4)) is a water molecule. Both aluminum atoms form typical octahedral coordination with oxygen (d_{ave}(Al(1)–O) = 1.945(6) Å, d_{ave}(Al(2)–O) = 1.902(6) Å), the selenium atom (d_{ave}(Se–O) = 1.711(5) Å; θ_{ave}(O–Se–O) = 96.4(3)°) is pyramidal, and three of

the four oxygen atoms form Al–O–Se bridges (θ_{ave} = 124.7(3)°). The selenite ion geometry compares well with the average values ($\langle d(\text{Se–O})\rangle$ = 1.709(10) Å, $\langle\theta(\text{O–Se–O})\rangle$ = 100.2(1.3)°; values in parentheses = r.m.s. deviations) recently derived by Hawthorne, Groat and Ercit (1987) for a large number of $(H)SeO_3$ species.

The structure of $Al_2(SeO_3)_3{\cdot}3H_2O$ consists of stacks of alternating Al(1) and Al(2) octahedra in the rhombohedral [111]-direction. Each Al(1) octahedron is linked to its nearest Al(2) neighbor by three different Al(1)–O(3)–Se(1)–O(2)–Al(2) links, thus forming an empty 'cage', centered at approximately $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$. The three O(1)s around Al(1) are also bonded to Se(1), thus adjacent octahedra of Al(1) are crosslinked by Al(1)–O(1)–Se(1)–O(3)–Al(1)′ and Al(1)–O(1)–Se(1)–O(2)–Al(2) links, building up an infinite network of octahedra and pyramids. $Al_2(SeO_3)_3{\cdot}3H_2O$ is isostructural with $Ga_2(SeO_3)_3{\cdot}3H_2O$ (Rastsvetaeva, Andrianov and Volodnia, 1986) and $Cr_2(SeO_3)_3{\cdot}3H_2O$ (Harrison, McManus, Stucky and Cheetham, 1991).

Two other aluminum selenite hydrate phases have been characterized by X-ray single crystal methods: $Al_2(SeO_3)_3{\cdot}6H_2O$ (AlSeO-I) and $Al(SeO_3)(HSeO_3){\cdot}2H_2O$ (AlSeO-II), which were also prepared under mild hydrothermal conditions (Morris, Harrison, Stucky and Cheetham, 1991), indicating the wealth of new systems accessible by these methods by subtle variation of reactant concentrations, *p*H and temperature. Both AlSeO-I and AlSeO-II contain 3-dimensional networks of octahedral aluminum cations and pyramidal selenium species, and both also contain Al–OH_2 links as part of the aluminum atom coordination. AlSeO-II has a quite different structure to $Al_2(SeO_3)_3{\cdot}3H_2O$, but AlSeO-I is closely related to the phase described here, and contains octahedral AlO_6 stacks joined by a similar triad of Al–O–Se–O′–Al′ bonds surrounding an empty cavity. However, in AlSeO-I, compared to $Al_2(SeO_3)_3{\cdot}3H_2O$, each terminal aluminum is coordinated to three waters as well the three oxo-selenium bridges to its neighbor. As opposed to $Al_2(SeO_3)_3{\cdot}3H_2O$, the third

Se–O vertex in AlSeO-I only partakes in H-bonds and is not associated with another aluminum cation. Thus 'molecular' units of $Al_2(SeO_3)_3 \cdot 6H_2O$ make up the repeating *motif* in AlSeO-I; in $Al_2(SeO_3)_3 \cdot 3H_2O$, three water molecules are eliminated, adjacent octahedral stacks shift relative to each other to form the Al–O–Se–O–Al crosslinking bonds described above, and a 3-dimensional, as opposed to molecular structure results. Investigation into related selenite phases is ongoing.

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* Lists of observed and calculated structure factors and aniostropic thermal parameters have been deposited with the British Library Document Supply Center as Supplementary Publication No. (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester, CH1 2HU, England.

Figure Caption.

Figure 1: Detail of the crystal structure of $Al_2(SeO_3)_3 \cdot 3H_2O$ showing the atomic labelling scheme and the linkage of Al(1) and Al(2) octahedra *via* selenite bridges. O(4) is a water molecule.

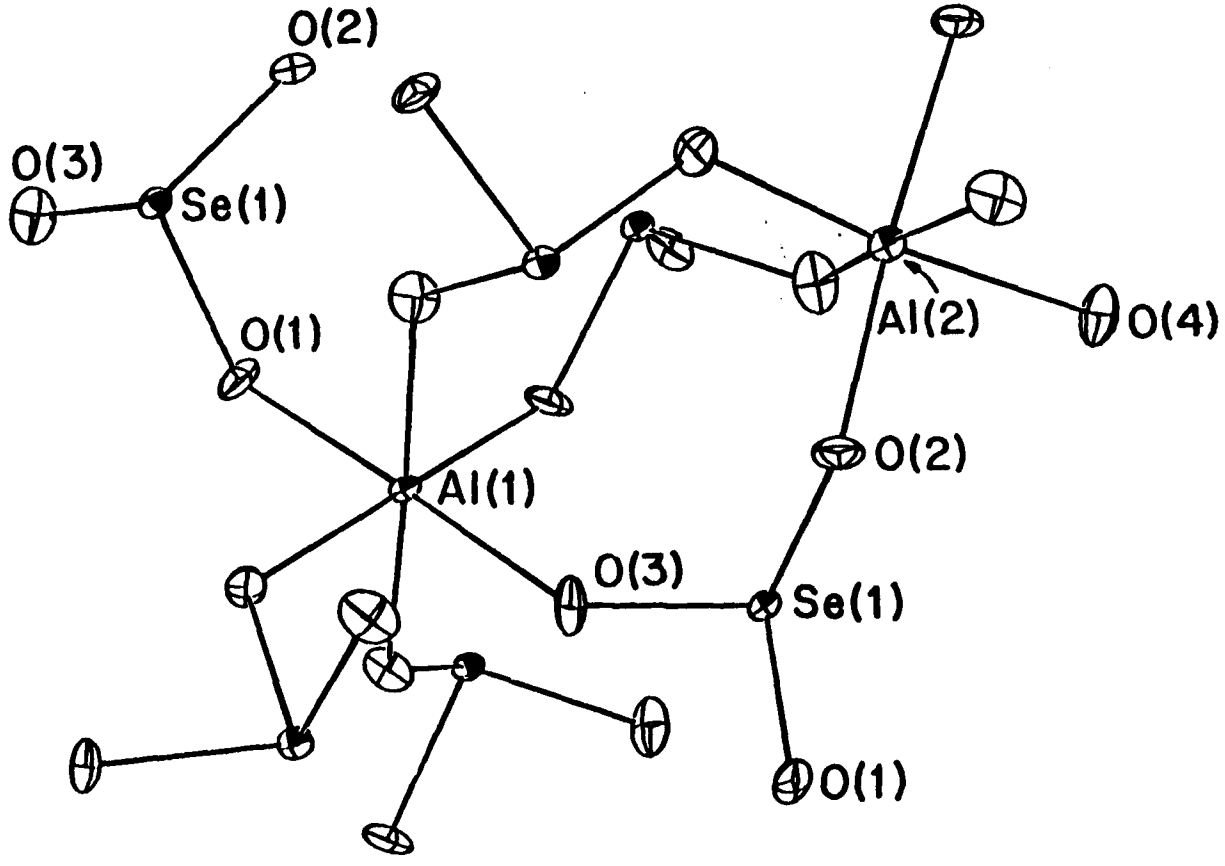
O(2)
O(3)
Se(1)
O(1)
Al(1)
Al(2)
O(4)
O(2)
O(3)
Se(1)
O(1)

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Table 1: Atomic Positional Parameters

$Al_2(SeO_3)_3 \cdot 3H_2O$

Atom	x	y	z	U_{equiv}
Al(1)	0.2048(3)	0.2048(3)	0.2048(3)	0.0052
Al(2)	0.4398(3)	0.4398(3)	0.4398(3)	0.0088
Se(1)	0.9188(2)	0.5458(2)	0.0086(2)	0.0067
O(1)	0.848(1)	0.594(1)	0.504(1)	0.0109
O(2)	0.204(1)	0.542(1)	0.423(1)	0.0136
O(3)	0.405(1)	0.310(1)	0.056(1)	0.0125
O(4)†	0.458(1)	0.690(1)	0.357(1)	0.0144

†water molecule

$U_{equiv} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

Table 2: Bond Distances(Å)/Angles(°)

$Al_2(SeO_3)_3 \cdot 3H_2O$

Al(1)–O(1)	1.958(8) × 3	Al(1)–O(3)	1.932(8) × 3
Al(2)–O(2)	1.836(8) × 3	Al(2)–O(4)	1.967(8) × 3
Se(1)–O(1)	1.699(7)	Se(1)–O(2)	1.754(8)
Se(1)–O(3)	1.679(7)		
O(1)–Al(1)–O(1)	91.5(4) × 3	O(3)–Al(1)–O(1)	87.6(3) × 3
O(3)–Al(1)–O(1)	86.6(3) × 3	O(3)–Al(1)–O(1)	177.9(4) × 3
O(3)–Al(1)–O(3)	94.3(4) × 3		
O(2)–Al(2)–O(2)	94.1(4) × 3	O(4)–Al(2)–O(2)	88.1(3) × 3
O(4)–Al(2)–O(2)	173.8(5) × 3	O(4)–Al(2)–O(2)	91.5(4) × 3
O(4)–Al(2)–O(4)	86.0(4) × 3		
O(2)–Se(1)–O(1)	100.5(4)	O(3)–Se(1)–O(1)	89.8(4)
O(3)–Se(1)–O(2)	98.8(4)		
Se(1)–O(1)–Al(1)	122.7(4)	Se(1)–O(2)–Al(2)	124.4(4)
Se(1)–O(3)–Al(1)	127.1(5)		

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